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Studies on the Solvent Effect of Aquo-n-Propanol Solvent Systems on the Catalysed Solvolysis of Aliphatic Decanoate Ester

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Abstract: The solvent effect of a primary alcohol namely n-propanol on the alkali catalysed solvolysis of reaction was studied by carrying out the hydrolysis of the ester having longer carbon chain namely Methyl decanoate in water-n-propanol media of varying composition consisting of 30 to 80% n-propanol (v/v) at different temperatures ranging from 20 to 40°C.

The specific rate constant values of the reaction were found to be depleted with increasing concentration of n-propanol in the reaction media. It was found that number of water molecules associated with the activated complex increases from 0.300 to 1.495 with increasing temperature from 20°C to 40°C and this tells about the fact that the bimolecular mechanistic path of the reaction is changed to unimolecular. The decrease and increase observed respectively in the values of iso-composition activation energy (E_C) and iso-dielectric activation energy (E_D) of the reaction show that the transition state is solvated and initial state is desolvated with addition of n-propanol in reaction media. From enhancement observed in values of ΔG* with simultaneous depletion in ΔH* and ΔS* values of the reaction, it has been concluded that the reaction is enthalpy stimulating and entropy inhibiting and specific solvation is taking place in the water-n-propanol media. From the evaluated values of iso-kinetic temperature, Le 284.80≈285 which is less than 300, it is inferred that this reaction in water-n-propanol media obeys Barclay-Butler rule and there is a weak but considerable solvent-solute interaction taking place in the reaction media.

Keywords: Catalysed Solvolysis, Depletion, Thermodynamic Activation Parameters, Activation energy, Enthalpy dominating. Entropy Controlled, Desolvation, Iso-kinetic Temperature, Associated, Barclay-Butler Rule, Solvent-Solute Interaction

I. INTRODUCTION

It has been proposed to study the kinetics of alkali catalysed hydrolysis of Methyl decanoate in water-n-propanol media as the study of solvent effect of higher primary alcohol, n-propanol on the perfume, fruit flavour and food additive producing biochemical efficiency of methyl decanoate has not been paid even a little attention by the kineticists so

far. So, it has been planned to perform the reaction in water-n-propanol media having varying concentration of n-propanol at 5 different temperatures i.e. at 20, 25, 30, 35 and 40°C in order to establish the mechanism of the reaction and also to study about the solvent-solute interaction in the reaction media, so that effect of higher primary alcohol (n-propanol) on the perfume, fruit flavour and food additive efficiency of methyl decanoate may be studied and highlighted for its day to day use for human beings.

A. Experimental

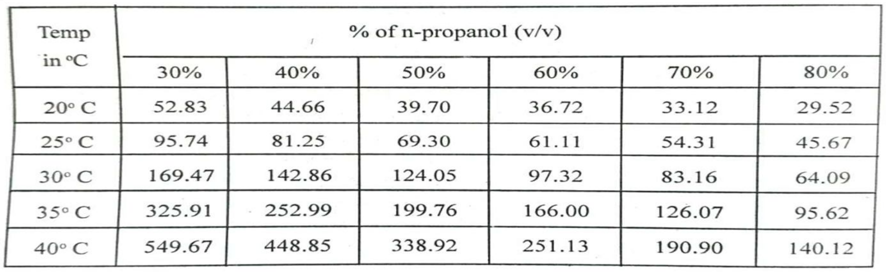
Export quality Methyl decanoate of Fluka ΔG* grade packed in Switzerland and n-propanol of Merck make were used. The kinetics of the reaction was studied as usual[1-4] by keeping the strength of alkali 0.1 M and that of the ester 0.5 M in the reaction mixture. The reaction was found to obey the second order kinetic equation and the evaluated values of specific rate constants have been recorded in Table-1. The variation of log k with log [H_2O] have been mentioned in Table - II and the evaluated values of number of water molecules associated with the activated complex have been tabulated in Table III. The numerical values of iso-composition and iso-dielectric activation energies (E_C and E_D) have been mentioned respectively in Table-IV and Table V. and the consolidated values of thermodynamic parameters i.e. ΔH* ΔG* and ΔS* calculated by using Wynne-Jones and Eyring[5] equation have been shown in Table-VI.

II. SOLVENT EFFECT ON THE RATE OF REACTION

From the data recorded in Table-l, it is clear that rate constant values of the reaction decrease with increasing proportion of n-propanol in the reaction media.

On plotting log k values against mole% of n-proanol as shown in Fig.-1, it is obvious that approximately up to 20 mol% of the n-proanol in the reaction media, the rate of the reaction falls rapidly but beyond.20 mol % of n-proanol, the depletion in the rate follows slow depleting path. However, the degree of depletion is found to be sharper with increase in temperature of the reaction. This decreasing trend in the values of rate constants needs to be discussed in the light Hughes and Ingold[6] predictions according to which an increase in the dielectric constant values of the reaction media causes an increase in the rate when there is concentration or construction of charges on the transition state and causes a decrease in the rate when there is diffusion or destruction of charges on the transition state. The values of dielectric constants of the reaction media go on decreasing with gradual addition of n-proanol. So our findings are not fully in accordance with the qualitative prediction of Hughes and Ingold. However, our findings are in agreement with the qualitative prediction of Laidler and Landskroener[7] and recent reports of Singh & Namrata et al[8], Kumar and Singh et al[9]. and Singh and Perween et al[10] who predicted that the rate of ion-dipolar reaction decreases with the decrease in the dielectric constant values of the reaction media. Overall, it has been concluded that the depletion in the rate of hydrolysis of Methyl decanoate in water-n-proanol media is due to both the dielectric effect of the reaction media and the solvation effect by the protic solvent n-proanol.

Table-1
Specific rate constant values of Alkali catalysed hydrolysis of
Methyl decanoate in water-n-propanol media
k x 10^3 in $(dm)^3$ $mole^{-1}$ min^{-1}



Temp in °C	% of n-propanol (v/v)					
	30%	40%	50%	60%	70%	80%
20° C	52.83	44.66	39.70	36.72	33.12	29.52
25° C	95.74	81.25	69.30	61.11	54.31	45.67
30° C	169.47	142.86	124.05	97.32	83.16	64.09
35° C	325.91	252.99	199.76	166.00	126.07	95.62
40° C	549.67	448.85	338.92	251.13	190.90	140.12

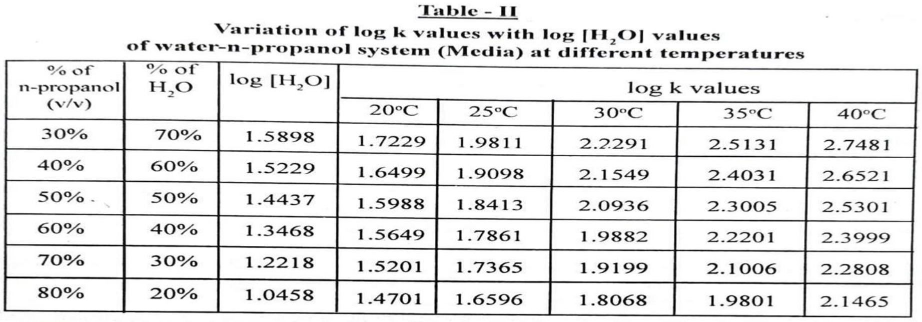


Table - II
Variation of log k values with log $[H_2O]$ values of water-n-propanol system (Media) at different temperatures

% of n-propanol (v/v)	% of H_2O	log $[H_2O]$	log k values				
			20°C	25°C	30°C	35°C	40°C
30%	70%	1.5898	1.7229	1.9811	2.2291	2.5131	2.7481
40%	60%	1.5229	1.6499	1.9098	2.1549	2.4031	2.6521
50%	50%	1.4437	1.5988	1.8413	2.0936	2.3005	2.5301
60%	40%	1.3468	1.5649	1.7861	1.9882	2.2201	2.3999
70%	30%	1.2218	1.5201	1.7365	1.9199	2.1006	2.2808
80%	20%	1.0458	1.4701	1.6596	1.8068	1.9801	2.1465

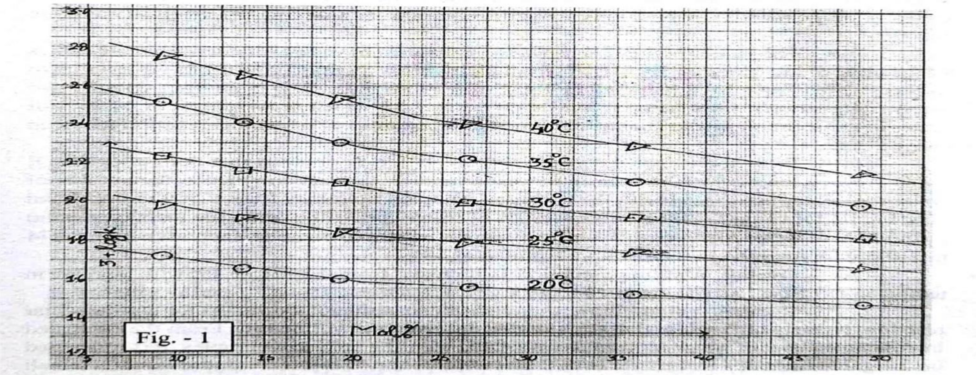


Fig. - 1

Fig. - 1 : Variation of log k values with mol % of n-propanol in water-n-propanol media

A. Solvent Effect on the Mechanistic pathway followed by the reaction

The effect of concentration of water [H_2O] of the water-n-proanol media (Mixture) on the rate and mechanism of alkali catalysed hydrolysis of Methyl decanoate has been studied in the guide lines and observations rendered by Tommila et al.[11] Lane[12] and Elsemongy et al[13]. They have established an idea of number of water molecules taking part in the formation of the activated complex. The number of water molecules associated with the activated complex using the relation proposed by Robertson[14] which is -

$$\log k = \log k_o + \log [H_2O]$$

where 'n' is the solvation number or number of water molecules associated with the activated complex of the reaction, which tells about the critarion for studying the mechanism of the reaction.

The values of number of water molecules (n) were evaluated from the slopes of the plots of log k versus log [H_2O] (from their values mentioned in Table - II) as shown in Fig. 2 and have been recorded in Table III. From Fig. 2, it is obvious that the two intersecting straight lines meet at log [H_2O] value 1.39 which corresponds to 44.20% of water in the reaction media at almost all the 5 temperatures at which the reaction has been carried out.

From the values recorded in Table III, it is obvious that before log [H_2O] value 1.39, i.e before 44.20% concentration of water in the reaction media, the number of water molecules associated with the activated complex increases from 0.300 to 0.853 and after log [H_2O] value 1.39 (i.e. after 44.20% of water concentration in the reaction media) the number of water molecules associated with the activated complex increases from 0.874 to 1.495 with increase in temperature from 20 to 40°C.

Overall, 'n' values are found to increase from 0.300 to 1.495with increase in temperature of the reaction from 20 to 40°C.

Robertson et al[15]. have established that value of slopes (n) for unimolecular reaction is fairly high while that for bimolecular reaction will be low. From the evaluated increasing number of water-molecules associated with the activated complex, it is concluded on the guide lines of Robertson et al[15] that in presence of n-propanol, the reaction alkali catalysed hydrolysis of Methyl decanoate changes its mechanistic pathway from bimolecular to unimolecular with increase in temperature of the reaction.

In the light of findings and report of Packer and Tomillinson[16] from increasing number of water molecules it is also concluded that in presence of n-propanol, water present in water-n-propanol media changes its structure from dense form to its bulky form with rise in temperature of the reaction from 20 to 40°C.

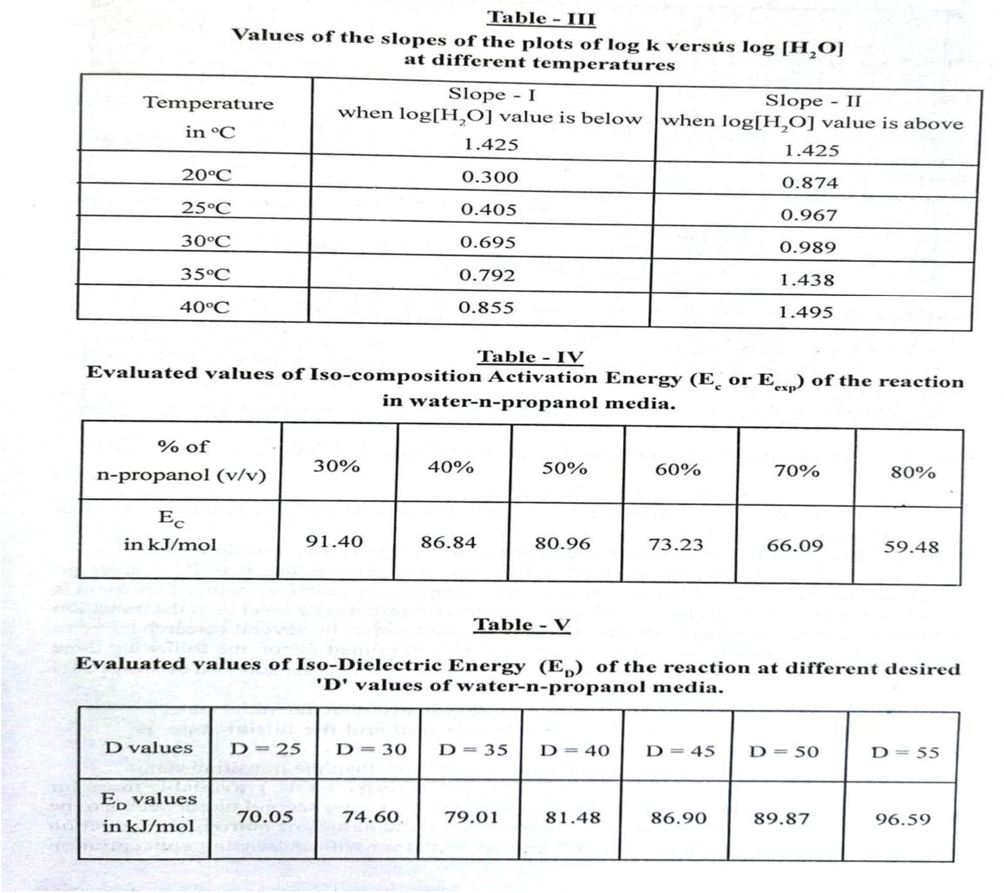


Table - III

Values of the slopes of the plots of log k versus log [H_2O] at different temperatures

Temperature in °C	Slope - I when log[H_2O] value is below 1.425	Slope - II when log[H_2O] value is above 1.425
20°C	0.300	0.874
25°C	0.405	0.967
30°C	0.695	0.989
35°C	0.792	1.438
40°C	0.855	1.495

Table - IV

Evaluated values of Iso-composition Activation Energy (E_c or E_{exp}) of the reaction in water-n-propanol media.

% of n-propanol (v/v)	30%	40%	50%	60%	70%	80%
E_C in kJ/mol	91.40	86.84	80.96	73.23	66.09	59.48

Table - V

Evaluated values of Iso-Dielectric Energy (E_D) of the reaction at different desired 'D' values of water-n-propanol media.

D values	D = 25	D = 30	D = 35	D = 40	D = 45	D = 50	D = 55
E_D values in kJ/mol	70.05	74.60	79.01	81.48	86.90	89.87	96.59

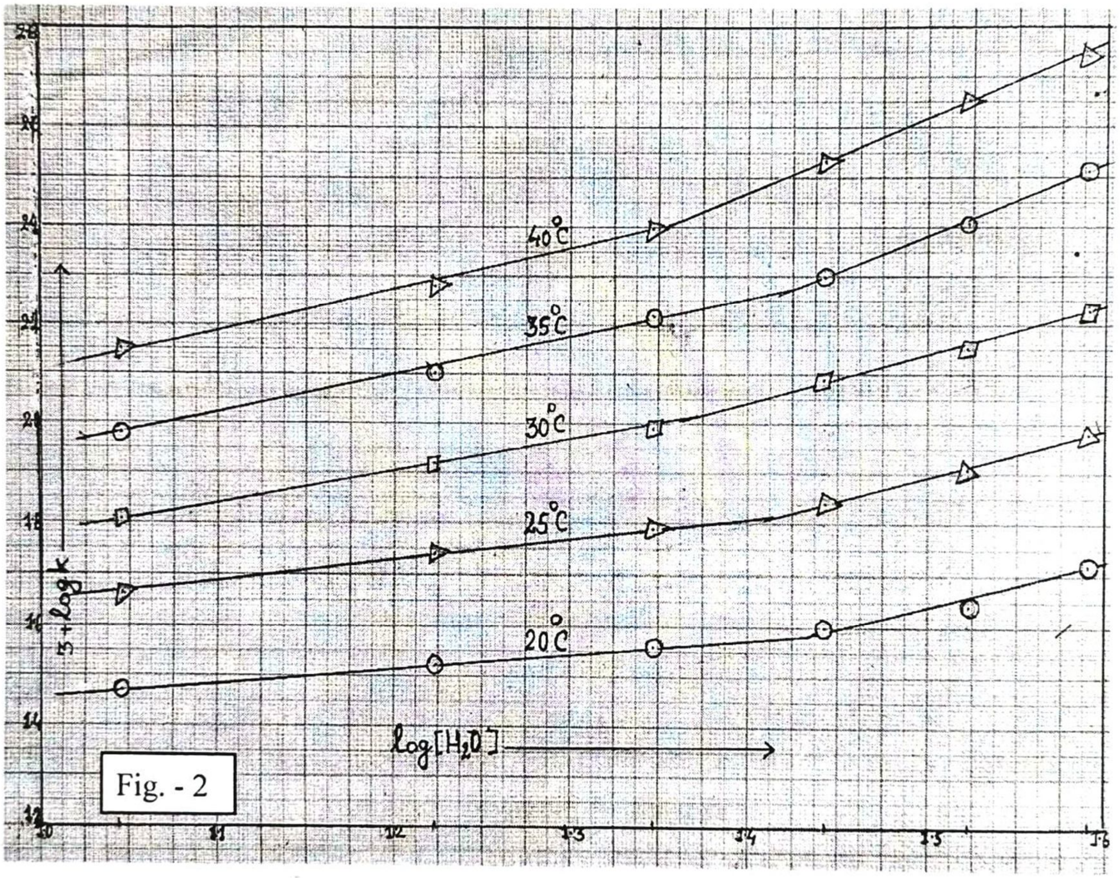


Fig. - 2

Fig. - 2 : Variation of log k values against log [H_2O] values in water-n-propanol media

$$(H_2O)_d \rightleftharpoons (H_2O)_b$$

Similar conclusions have also been reported recently by Kumar & Singh et al[17] and Singh & Singh et al[18]

B. Solvent Effect on the Iso-composition Activation Energy of the reaction

From the values recorded in Table-IV, it is obvious that E_c or E_{exp} values go on decreasing with increasing concentration of n-propanol in reaction media. This trend is probably due to solvation changes taking place either at initial state level or at the transition state level or at the level of both the states as reported earlier by several researchers[19,20] in this field. Considering the extent of solvation to be a dominant factor, the following three factors seem to be responsible for decrease in E_c values with gradual addition of n-propanol in the reaction media:-

(1) The transition state is more solvated than the initial state.

(2) The transition state is solvated and the initial state is desolvated, and

(3) The initial state is more desolvated than the transition state.

The transition state being large anion (ester + OH) available more for solvation by n-propanol molecule than the initial state, so the second factor seems to be operative in our case and it also gets support when the values of entropy of activation (ΔS^*) and enthalpy of activation (ΔH^*) go on depleting with increasing concentration of n-propanol (Table- VI). Similar depletion in the values of activation energy of the reaction with gradual addition of the organic content in the reaction media has also been reported recently by the researchers of the group of Singh et al[21,22].

C. Solvent effect on the Iso-dielectric Activation Energy of the Reaction

On perusal of the data mentioned in Table - V, it is clear that the value of iso-dielectric activation energy (E_D) of the reaction are found to increase with increasing dielectric constants of water-n-propanol media. ΔS* dielectric constants of water-n-propanol media decrease with addition of the organic solvent (n-propanol) to it, so in other way it may be concluded that like iso-composition activation energy, the values of iso-dielectric activation energy of the alkali catalysed hydrolysis of Methyl decanoate in water-n-propanol media are also decreasing with gradual addition of n-propanol in the reaction media.

The E_D value is 70.05 kJ/mol at D-25 and enhances to 96.59 kJ/mol at D = 55. This trend of variation is in good agreement with that of Wolford[23].

However, such variation in E_D values of the reaction with increasing D values of the reaction media has also been supported by the recent findings of Singh & Perween[3], Kumar & Singh et al[24]. and Singh & Singh et al[25].

D. Solvent effect on Thermodynamic Activation Parameters of the reaction:

For better study of the effects of solvent, the thermodynamic activation parameters, such as enthalpy of activation ΔH*, entropy of activation ΔS* and free energy of activation ΔG* were taken into account as they have great significance. These parameters were evaluated using Wynne-Jones and Eyring[5] equation have been recorded in Table- VI.

In order to highlight the effect of solvent concentration on these thermodynamic parameters more clearly, ΔH*, ΔG* and ΔS* values were plotted against mole% of n-propanol which are shown in figures 3, 4 and 5 respectively.

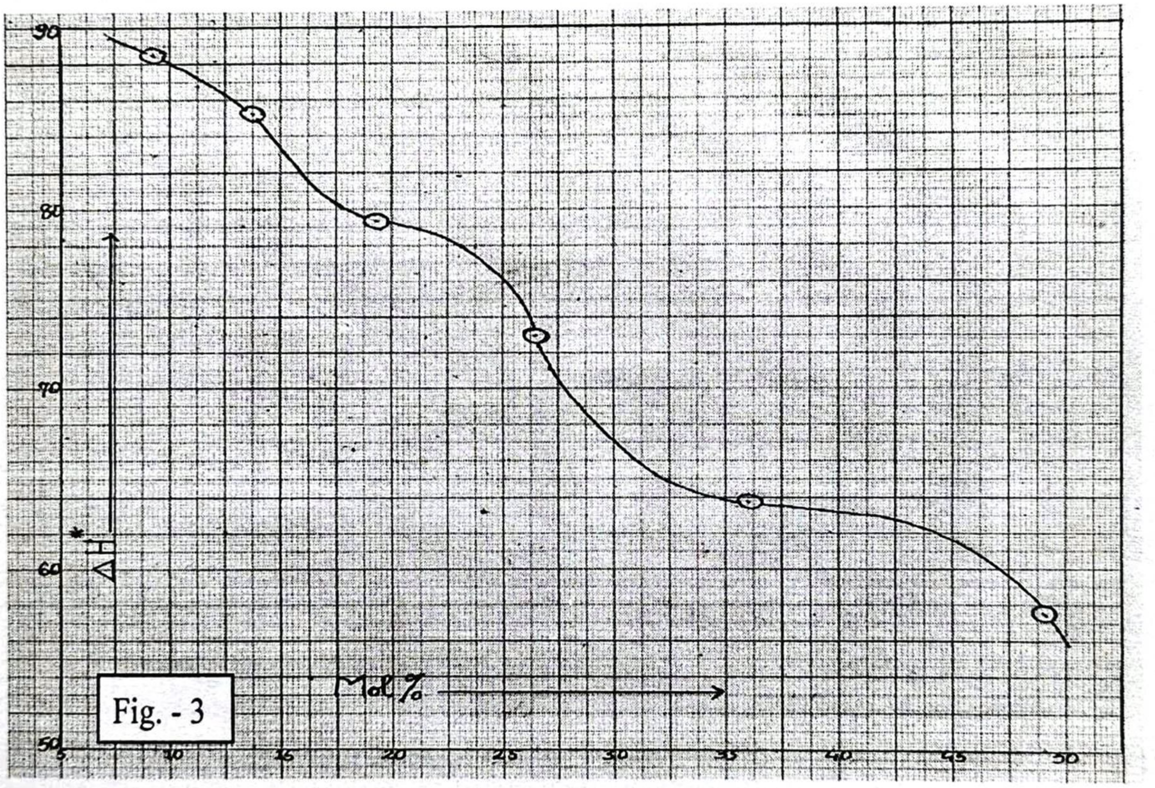


Fig. - 3 : Variation of ΔH* values with mol % of n-propanol in water-n-propanol media

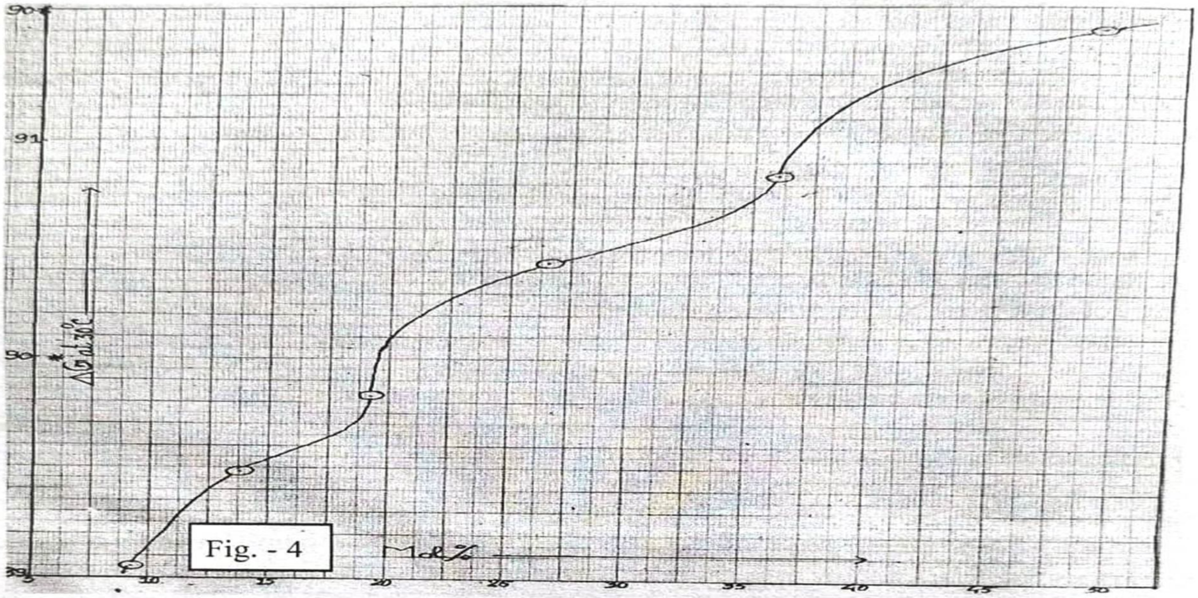


Fig. - 4: Variation of ΔG* values with mol % of n-propanol in water-n-propanol media

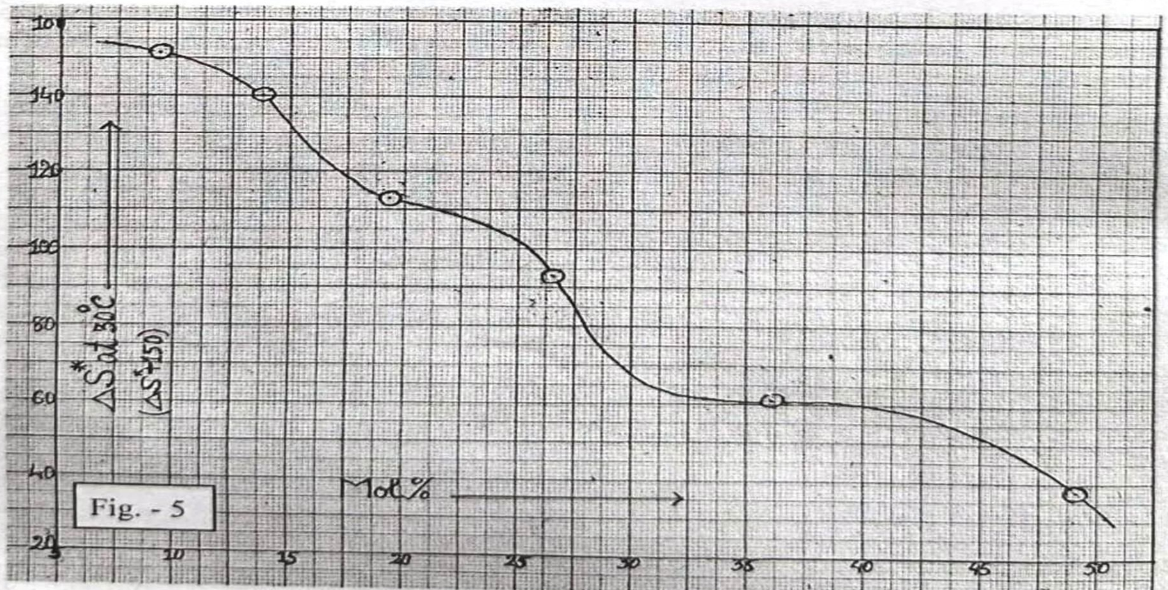


Fig. -5 : Variation of ΔS* values with mol % of n-propanonl in water-n-propanol media

From Fig.-4 and the values of ΔG* recorded in Table-V obviously indicate that the variation in ΔG* is small and it increases from 89.05 to 91.50 kJ/mol with change of proportion of n-propanol from 30% to 80% (v/v) at 30 deg * C slowly with gradual addition of the organic constant in water. The small but considerable increase in ΔG* and non-linear variation in ΔH* and ΔS* curves with the increasing mol% of n-propanol as shown in Figs. -3 and 5, are indication of specific solvation taking place in the process of activation as already reported by Saville & Hudson[26] and Tomilla et al.[27], Elsemongy et al.[13] and Cleve have also observed the similar increase in ΔG* values. Increase in ΔG* with simultaneous decrease in ΔH* and ΔS* values are only possible when the extent (degree) of depletion in ΔS* values is greater than that in ΔH* values and from this, it may be inferred that in alkali catalysed hydrolysis of Methyl decanoate in water-n-propanol media, n-propanol acts as entropy inhibitor and enthalpy stimulator solvent. Such inferences have also recently been supported by the recent views of Kumar & Singh[29] and Singh et al[30].

E. Obedience of Barklay-Butler relationship and Solvent Effect on Solvent-solute Interaction

This reaction is found to obey Barclay-Butler[31] relationship as a straight line is obtained when ΔH* values are potted against ΔS* values at 30°C (values mentioned in Table-VI) as shown in Fig.-6 and from the value of the slope of the plot, the evaluated values of iso-kinetic temperature of the reaction comes to be 284.8 ≈ 285 In the light of the reports of Leffler[32], low but considerable value of iso-kinetic temperature shows that in presence of n-propanol, there is weak but appreciable solvent-solute interaction in the reaction media (water-n-propanol). Similar findings and interpretations have also recently been reported by Singh & Perween[3] and Kumar & Singh[33].

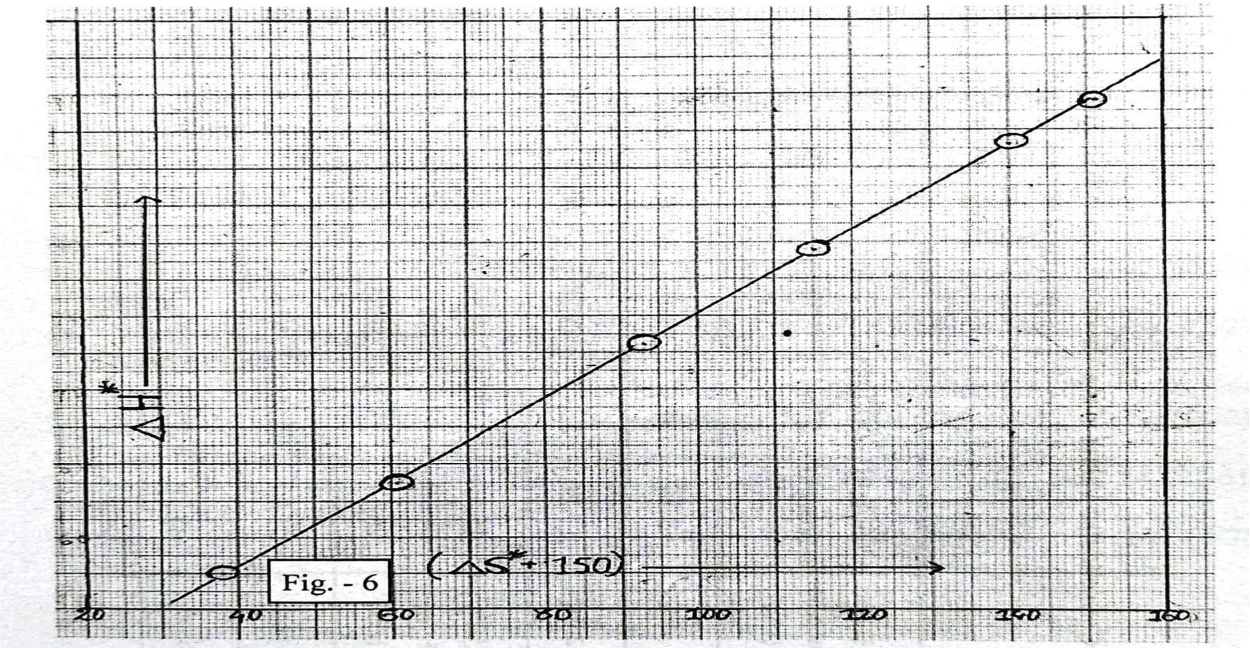


Fig. - 6 : Plots of ΔH* values against ΔS* values in water-n-propanol media

Table - VI

Consiolidated Values of the Thermodynamic Activation Parameters (ΔH*, ΔG* and ΔS*) of the reaction in water - n-propanol solvent systems at different temperatures

ΔH* and ΔG* in kJ/mol, ΔS* in J/K/mol

% of n-propanol (v/v)	Mol % of n-propanol	ΔH* in kJ/mol	20°C		25°C		30°C		35°C		40°C	
			ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*	ΔG*	ΔS*
30%	9.33	89.47	88.87	2.06	88.95	1.74	89.05	1.40	88.88	1.90	88.96	1.63
40%	13.79	86.43	89.28	−9.70	89.36	−9.82	89.45	−10.05	89.47	−9.88	89.54	−9.91
50%	15.35	79.40	89.56	−34.69	89.75	−34.73	89.83	−34.44	90.08	−34.68	90.27	−34.72
60%	26.47	73.03	89.75	−57.06	90.06	−57.15	90.44	−57.46	90.61	−57.07	91.05	−57.55
70%	35.90	63.82	90.00	−89.36	90.35	−89.01	90.84	−84.17	91.32	−89.25	91.76	−89.26
80%	48.98	57.51	90.28	−111.85	90.79	−111.65	91.50	−112.16	92.03	−112.06	92.56	−111.99

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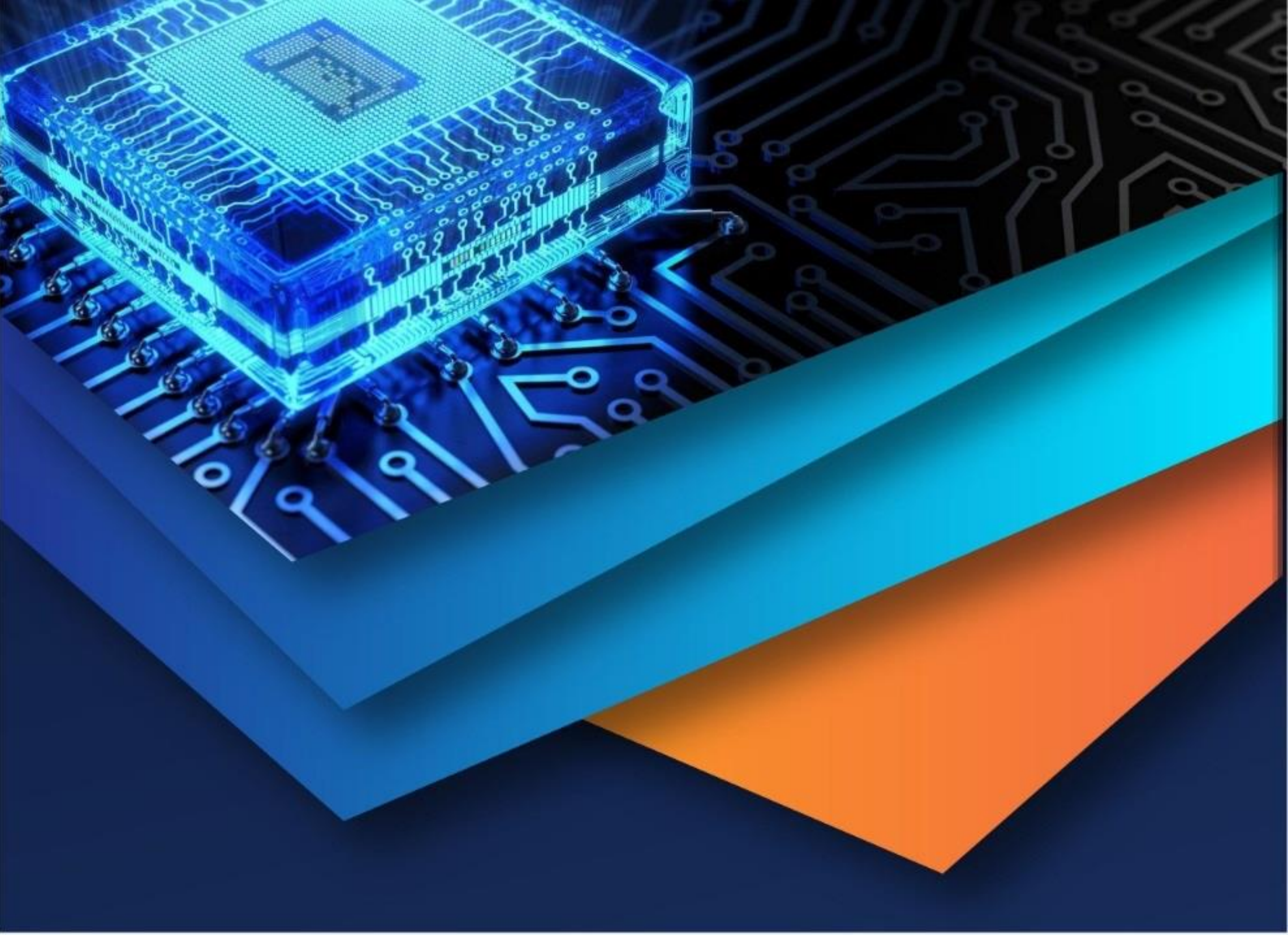

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